

## PATENT ABSTRACTS OF JAPAN

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## (54) ADDITIVE FOR PAPERMAKING

## (57)Abstract:

PURPOSE: To provide the additive containing a (meth)acrylamide copolymer of graft structure, excellent in papermaking workability, having excellent effects such as paper strengthening and water filterability improvement.

CONSTITUTION: The objective additive for paper making a contains a graft copolymer which can be obtained by grafting between a copolymer I from (A) acrylamide and/or methacrylamide, (B) an anionic vinyl monomer and (D) a crosslinkable vinyl monomer and a copolymer II from the component A, (C) a cationic vinyl monomer and the component D. This graft copolymer has the following characteristics: (1) weight-average molecular weight: 1000000-5000000, (2) the ratio of the viscosity of its aqueous solution at a concentration of 15wt.% at pH 4-9 to that of its aqueous solution at the same concentration at pH 2-3.5 is 1.5-6, and (3) its viscosity rises at pH 4-9 in papermaking process, forming a robust polyion complex at pH 4-9; thus enabling high setting with pulp fibers, high paper strength and water filterability raising without disturbing formations.

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CLAIMS

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[Claim(s)]

[Claim 1] (a) The copolymer which comes to copolymerize (d) cross-linking vinyl monomer in acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list as a principal component (I), (a) Acrylamide and/or methacrylamide, (c) cationic vinyl monomer, It is the graft copolymer which comes to carry out the graft of the copolymer (II) which comes to copolymerize (d) cross-linking vinyl monomer as a principal component to a list. The additive for paper manufacture which the weight average molecular weight of this graft copolymer is 1 million-5 million, and comes to contain the graft copolymer whose ratios of the viscosity in pH 4-9 in this concentration are 1.5-6 to the viscosity in pH 2-3.5 in 15% concentration of this graft copolymer water solution.

[Claim 2] The additive for paper manufacture according to claim 1 with which the water solution of said graft copolymer forms the poly ion complex by pH 4-9.

[Claim 3] The additive for paper manufacture according to claim 1 whose cross-linking vinyl monomer (aforementioned [ d ]) is a vinyl monomer which has a chain transfer nature substituent in a side chain.

[Claim 4] (a) The manufacture approach of the additive for paper manufacture according to claim 1 characterized by carrying out the graft copolymerization of the copolymer (II) which becomes (a) acrylamide and/or methacrylamide, (c) cationic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component after copolymerizing the copolymer (I) which becomes acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component.

[Claim 5] (a) The manufacture approach of the additive for paper manufacture according to claim 1 characterized by carrying out the graft copolymerization of the copolymer (I) which becomes (a) acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component after copolymerizing the copolymer (II) which becomes acrylamide and/or methacrylamide, (c) cationic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component.

[Claim 6] The paper-making approach characterized by carrying out paper making after adding the additive for paper manufacture according to claim 1 to 3 on condition that pH 4-9 to a pulp slurry.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the additive for paper manufacture. In detail, it is related with the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of graft structure.

[0002]

[Description of the Prior Art] In recent years, on the occasion of manufacture of paper and the paper board, importance has been attached to the additive for paper manufacture, especially the paper reinforcing agent. It is further raised with the purpose of energy saving or a deployment of a resource that use of good-quality pulp was restricted with aggravation of a bolt supply situation as this background and that the need for reuse of used paper became strong much more, and the additive for paper manufacture as a modifier of paper and the paper board is much more indispensable as that result.

[0003] On the other hand, the dependence and its use range of a filtration improvement agent and a paper reinforcing agent have spread further for the purpose of upgrading according to the improvement in the productivity accompanying improvement in the speed of a paper machine, or diversification of paper. As an additive for paper manufacture, a polyacrylamide system is in use under this situation.

[0004] The additive for polyacrylamide system paper manufacture can be classified into an anion type, a cation type, and a both-sexes type according to ionicity. For example, as this anion type, the partial hydrolysate of a copolymer with alpha [ which is acrylamide and an anionic vinyl monomer ], beta-partial saturation monocarboxylic acid or alpha, and beta-partial saturation dicarboxylic acid, or an acrylamide system copolymer etc. is known. On the other hand, as a cation type and a both-sexes type, there is a denaturation type and copolymerization type thing based on a difference of the introductory approach of an ionicity functional group. For example, as a denaturation type, there are a Hofmann rearrangement object of an acrylamide system copolymer, a MANNIHHI denaturation object, etc., and, on the other hand, the various copolymers which come to copolymerize a cationic vinyl monomer and the Nonion nature vinyl monomer which an anionic vinyl monomer or others may copolymerize acrylamide (meta) and if needed as a copolymerization type are known (JP,60-94697,A).

[0005] however, conventionally well-known in recent years, since the service condition of the additive for paper manufacture is becoming still severer -- it is coming to the limitation by the additive for polyacrylamide system paper manufacture of low molecular weight in respect of the effectiveness as an additive comparatively. Therefore, the means of macromolecule quantification is taken in order to aim at improvement in the engine performance, but since the viscosity of the copolymer obtained rises too much when macromolecule quantification is only carried out, the dispersibility at the time of paper making serves as a defect. Consequently, when this copolymer is used as an additive for paper manufacture, too much condensation arises, and it is easy to cause the conditions turbulence of perfect paper.

[0006] Although the attempt to which you are going to make it increase that molecular weight was made suppressing a viscosity rise of the copolymer obtained, the effectiveness as an

additive for paper manufacture was not [ that this trouble should be canceled / that it is hard to introduce branching structure uniform in the reactivity of a cross linking agent being inadequate ] yet enough [ branching structure was given by using a cross linking agent, and ]. Moreover, although the approach of using the water solution which comes to mix the anionic Pori (meta) acrylamide and cationic Pori (meta) acrylamide of low molecular weight beforehand comparatively was also proposed, the effectiveness as an additive for paper manufacture was not yet enough. [0007]

[Problem(s) to be Solved by the Invention] This invention comes to contain the acrylamide (meta) system copolymer of the amount of macromolecules, and aims at offering the additive for paper manufacture whose engine performance is hypoviscosity comparatively and moreover improved by excelling in fixable [ to pulp ].

[0008]

[Means for Solving the Problem] The result of having repeated research wholeheartedly this invention persons solving the technical problem of said conventional technique, According to the acrylamide (meta) system copolymer of the graft structure of the both-sexes type which gave the bias to the ion component which consists of an anionic polymer part and a cationic polymer part According to the copolymer of this graft structure, further it not only can obtain, without making the acrylamide (meta) system copolymer of the amount of macromolecules hyperviscosity-ize, but Viscosity changes depending on pH and from viscosity rising by 4-9 which are paper making pH when it is hypoviscosity by pH 2-3.5 notably This copolymer came to complete a header and this invention for excelling in fixable [ to pulp ] and excelling in many effectiveness, such as paper durability enhancement as an additive for paper manufacture, and filtration improvement.

[0009] Namely, the copolymer with which this invention comes to copolymerize (d) cross-linking vinyl monomer in (a) acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list as a principal component (I), (a) Acrylamide and/or methacrylamide, (c) cationic vinyl monomer, It is the graft copolymer which comes to carry out the graft of the copolymer (II) which comes to copolymerize (d) cross-linking vinyl monomer as a principal component to a list. The weight average molecular weight of this graft copolymer is 1 million-5 million. And the ratio of the viscosity in pH 4-9 in this concentration starts the additive for paper manufacture which comes to contain the graft copolymer which are 1.5-6 to the viscosity in pH 2-3.5 in 15% concentration of this graft copolymer water solution.

[0010] In this invention, although it can be independent-used or the acrylamide or methacrylamide which is the (a) component can be used together, it is good to carry out independent use of the acrylamide from the field of economical efficiency.

[0011] As an anionic vinyl monomer which is the aforementioned (b) component, the sodium salt of organic sulfonic-acids [ , such as dicarboxylic acid; vinyl sulfonic acids, such as monocarboxylic acid; maleic acids, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a fumaric acid, an itaconic acid, muconic acid and a citraconic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, ]; or these various organic acids, potassium salt, etc. are raised, for example. moreover, as a cationic vinyl monomer (c) For example, dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, Dimethylaminopropyl (meta) acrylamide, diethylamino propyl (meta) acrylamide, The vinyl monomers which have the third class amino groups, such as allylamine, a diaryl amine, or a triaryl amine, or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content vinyl monomer and methyl chloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the fourth class-ized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised. These ionicity vinyl monomer is independent in a kind, or can use two or more sorts together.

[0012] (d) As a cross-linking vinyl monomer which is a component For example, ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as hexa methylenebis (meta) acrylamide

Divinyl ester, such as an adipic-acid divinyl and a sebacic-acid divinyl Allyl compound methacrylate, epoxy acrylate, and urethane acrylate N-methylol acrylamide, a diaryl amine, diaryl dimethylammonium, 2 functionality vinyl monomers, such as diallyl phthalate, diallyl chloroendate, and a divinylbenzene, 1, 3, 5-thioria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, 3 functionality monomers, such as triaryl amine, triallyl trimellitate, N, and N-diaryl acrylamide, 4 functionality vinyl monomers, such as tetramethylolmethane tetraacrylate, tetra-allyl compound pyromellitate, N and N, N', and N'-tetra-allyl compound-1,4-diaminobutane, a tetra-allylamine salt, and tetra-allyloxy ethane, etc. are raised.

[0013] Moreover, as a cross-linking vinyl monomer of this invention, the vinyl monomer which has a chain transfer nature substituent can be used. As a vinyl monomer which has a chain transfer nature substituent, if it has a chain transfer nature functional group, a vinyl monomer, itaconic-acid diester, etc. which can use it without a limit, for example, have an allyl group, a polyalkylene glycol radical, N-permutation amide group, etc. will be raised especially. As a vinyl monomer which has an allyl group, allyl compound (meta) acrylate, N-allyl compound (meta) acrylamide, N, and N-diaryl (meta) acrylamide etc. is mentioned. Moreover, the thing to about ten repeat units can usually be used that what is necessary is just what has the repeat unit of at least two oxy-alkylene groups as a polyalkylene glycol radical. As an example, diethylene-glycol monochrome (meta) acrylate, Polyethylene-glycol monochrome (meta) acrylate, such as triethylene glycol monochrome (meta) acrylate and tetraethylene glycol monochrome (meta) acrylate, Said same polypropylene-glycol monochrome (meta) acrylate, methoxy polyethylene-glycol monochrome (meta) acrylate, Poly trimethylene-glycol monochrome (meta) acrylate, polytetramethylene glycol monochrome (meta) acrylate, polyethylene-glycol propylene glycol monochrome (meta) acrylate, etc. are raised. Moreover, as a vinyl monomer which has N-permutation amide group etc., dimethyl acrylamide, diacetone acrylamide, isopropyl acrylamide, 2-acrylamido-2-methyl propane sulfonic acid, a 2-acrylamide-isobutane carboxylic acid, the alkyl ester of these carbon numbers 1-4, etc. are raised. Moreover, as itaconic-acid diester, the dialkyl ester of the itaconic acid of carbon numbers 1-4 is raised.

[0014] Although all can be used in this invention if it is said cross-linking vinyl monomer, it is desirable to use the vinyl monomer which has a chain transfer nature substituent in respect of a paper durability enhancing effect. Moreover, a cross-linking vinyl monomer may use one sort, and may use two or more sorts.

[0015] The additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of the graft structure of this invention is manufactured by the approach shown below.

[0016] (1) The approach of carrying out copolymerization (graft) of the copolymer (II) which becomes (a) acrylamide and/or methacrylamide, (c) cationic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component, after copolymerizing the copolymer (I) which becomes (a) acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component.

[0017] (2) The approach of carrying out copolymerization (graft) of the copolymer (I) which becomes (a) acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component, after copolymerizing the copolymer (II) which becomes (a) acrylamide and/or methacrylamide, (c) cationic vinyl monomer, and a list considering (d) cross-linking vinyl monomer as a principal component.

[0018] First, the amount of the various components used used for the above (1) and the graft polymerization method of (2) is explained. As opposed to the total mol sum of the monomer component from which the (a) component used for the polymerization of a copolymer (I) constitutes a copolymer (I) usually, about 60-99 mol % -- desirable -- 70-96-mol % and the (b) component -- the same -- usually -- about 0.5-20 mol % -- desirable -- 2 - 15-mol % and the (d) component -- the same -- about 0.005-0.5 mol % -- it may be 0.01 - 0.3-mol % preferably. As opposed to the total mol sum of the monomer component from which the (a) component used for the polymerization of a copolymer (II) constitutes a copolymer (II) on the other hand (a) -- a component -- usually -- about 60-99 mol % -- desirable -- 70 - 96-mol % and the (c) component -- the same -- usually -- about 0.5-20 mol % -- desirable -- 2 - 15-mol % and the

(d) component -- the same -- about 0.005–0.5 mol % -- it may be 0.01 – 0.3–mol % preferably. [0019] In addition, although the graft copolymer of this invention is characterized by having a bias like ion with anionic [ of a copolymer (I) ], and the cationicity of a copolymer (II) It does not bar carrying out little concomitant use of the (c) component in the polymerization of a copolymer (I) within limits which do not spoil the purpose of this invention, and does not bar carrying out little concomitant use of the (b) component in the polymerization of a copolymer (II) within limits which do not spoil the purpose of this invention.

[0020] Moreover, in addition to said principal component, (e) Nonion nature vinyl monomer can be further used for the graft copolymer of this invention. (e) the total mol sum of the monomer component which constitutes a copolymer (I) if the amount of the component used is in a copolymer (I) -- receiving -- usually -- or less about 25 mol % -- it is less than [ 15 mol % ] preferably. moreover, the total mol sum of the monomer component which constitutes a copolymer (II) if the amount of the (e) component used is in a copolymer (II) -- receiving -- usually -- or less about 25 mol % -- it is less than [ 15 mol % ] preferably.

[0021] As the Nonion nature vinyl monomer (aforementioned [ e ]), the alkyl ester of the anionic vinyl monomer (aforementioned [ b ]), acrylonitrile, styrene, vinyl acetate, the methyl vinyl ether, etc. are raised, for example.

[0022] moreover, use mole-ratio (I)/(II) of the vinyl monomer which constitutes said copolymer (I) and copolymer (II) -- the range of 1 / 5 – 5/1 -- what is necessary is just to adjust each configuration monomer that what is necessary is just 1 / 3 – 3/1 preferably, so that it may become said amount used by this within the limits

[0023] Manufacture of the graft copolymer of this invention can be conventionally performed by various well-known approaches. For example, the vinyl monomer and water which constitute the above-mentioned copolymer (I) (or copolymer (II)) are first taught to a predetermined reaction container. The initiator of persulfate systems, such as potassium persulfate and ammonium persulfate, or the redox system polymerization initiator of the form which combined these persulfate and the reducing agent like a sodium hydrogensulfite, Or the usual radical polymerization initiators, such as an initiator of an azo system, are added, and chain transfer agents, such as isopropyl alcohol and allyl alcohol, are used suitably if needed, and a water-soluble desired acrylamide system copolymer is manufactured by warming under churning. Then, by dropping the vinyl monomer which constitutes a copolymer (II) (or copolymer (I)) in the system containing the water-soluble acrylamide system copolymer of a copolymer (I) (or copolymer (II)), copolymerization can be performed and a desired graft copolymer can be obtained. Polymerization temperature usually has good about 70–100 degrees C.

[0024] The molecular weight of the graft copolymer obtained in this way is usually 1 million to about 5 million. If a paper durability enhancing effect is especially taken into consideration, it is desirable that it is 1,500,000 or more.

[0025] Moreover, the graft copolymer of this invention is characterized by the ratios of the viscosity in pH 4–9 in this concentration being 1.5–6 to the viscosity in pH 2–3.5 in 15% concentration. The viscosity in pH 2–3.5 in 15% concentration is specifically 1000–10000cps, and viscosity is 1500–60000cps by pH 4–9 in this concentration. Moreover, it is also the description that the water solution of said graft copolymer forms the poly ion complex by pH 4–9.

[0026] Therefore, since the graft copolymer of this invention has the comparatively low viscosity of the product which is about two to 3.5 pH, its distributed condition as an additive for paper manufacture is good. Therefore, filterability improvement and improvement in paper durability can be aimed at with this additive, without being able to distribute the additive for paper manufacture in a paper-making system to homogeneity, and causing formation turbulence. Moreover, only in the paper making pH of pH 4–9, since viscosity also goes up while becoming the amount of macromolecules seemingly only in paper making pH in order to form the poly ion complex, the graft copolymer of this invention can aim at filterability improvement which was excellent especially within the paper-making system, and improvement in paper durability.

[0027]

[Effect of the Invention] The additive for paper manufacture which comes to contain the acrylamide system copolymer which has the graft structure of this invention (meta) is the

copolymer of the amount of macromolecules in hypoviscosity, and shows the outstanding workability in paper making. moreover, in 4-9 which are paper making pH, that viscosity increases and since the firm poly ion complex is further formed in pH 4-9, the graft copolymer of this invention can raise [ high fixing of a between / pulp fiber / , high paper durability reinforcement, and ] filterability, without disturbing conditions further -- etc. -- the various characteristic engine performance as an additive for paper manufacture is shown.

[0028]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. In addition, each of sections and %s is based on weight criteria.

[0029] The ion-exchange-water 509 section was taught to the 6 opening flask equipped with example 1 agitator, a thermometer, a reflux cooling pipe, two dropping funnels, and nitrogen gas installation tubing, the oxygen in the system of reaction was removed in it through nitrogen gas, and the temperature up was carried out to it to 100 degrees C.

[0030] Subsequently, as a monomer I, the acrylamide 95.5 section, the ion-exchange-water 304 section, the 50% sulfuric-acid 11.7 section, the dimethylaminoethyl methacrylate 23.4 section, and the dimethyl acrylamide 0.2 section were taught to the dropping funnel, and the oxygen in the system of reaction was removed through nitrogen gas.

[0031] Moreover, to another dropping funnel, as a monomer II, the acrylamide 95.5 section, the ion-exchange-water 304 section, the 80% acrylic-acid water-solution 13.4 section, and the dimethyl acrylamide 0.2 section were taught, and the oxygen in the system of reaction was removed through nitrogen gas.

[0032] Moreover, the ammonium persulfate 0.5 section and the ion-exchange-water 90 section were taught to another dropping funnel as a polymerization initiator.

[0033] While keeping the inside of a system at 95-100 degrees C and dropping the polymerization initiator at the bottom of churning of 300rpm, after dropping and carrying out copolymerization of the above-mentioned monomer I, the above-mentioned monomer II was dropped and the polymerization was performed for 2 hours. It cooled after 1-hour incubation. The description at the time of Table 2 and about five pH is shown for the description at the time of about three pH of the obtained copolymer water solution in Table 3.

[0034] In two to example 4 example 1, among the class of (a) component - (e) component, or its amount used, in any, at least one sort was changed, as shown in Table 1, and also the same actuation as an example 1 was performed, and the graft copolymer water solution was obtained. The description according to pH of each obtained copolymer water solution is shown in Table 2 and 3. In addition, a visual judgment of the condition at the time of diluting the obtained copolymer water solution to concentration 1% was made with "1% concentration" of Table 2 and 3.

[0035] In one to example of comparison 4 examples 1-4, the polymerization of the monomer of Monomer I and Monomer II was carried out to coincidence, and also the same actuation as an example 1 was performed. The description according to pH of the obtained copolymer water solution is shown in Table 2 and 3.

[0036]

[Table 1]

表 1

		組 成 (モル%)				
		(a)	(b)	(c)	(d)	(e)
実施例 1	モノマー I	AM 88.8	—	DM 10.1	DMAA 0.1	—
	モノマー II	AM 89.9	AA 10.0	—	DMAA 0.1	—
実施例 2	モノマー I	AM 84.9	—	DM 10.0	DMAA 0.1	AN 5.0
	モノマー II	AM 84.9	AA 10.0	—	DMAA 0.1	AN 5.0
実施例 3	モノマー I	AM 85.0	—	DMAA 9.9	DMAA 0.1	—
	モノマー II	AM 84.9	AA 10.0	—	DMAA 0.1	—
実施例 4	モノマー I	AM 85.0	—	DMAA 9.9	DMAA 0.1	AN 5.0
	モノマー II	AM 84.9	AA 10.0	—	DMAA 0.1	AN 5.0
比較例 1	—	AM 89.9	AA 5	DM 5	DMAA 0.1	—
比較例 2	—	AM 84.9	AA 5	DM 5	DMAA 0.1	AN 5
比較例 3	—	AM 89.9	AA 5	DMAA 5	DMAA 0.1	—
比較例 4	—	AM 84.9	AA 5	DMAA 5	DMAA 0.1	AN 5

[0037] the inside of Table 1, and AM -- acrylamide -- DM -- dimethylaminoethyl methacrylate -- DMAPAA -- dimethylaminopropyl acrylamide -- in AA, DMAA shows dimethyl acrylamide and AN shows acrylonitrile for an acrylic acid, respectively. Moreover, each monomer I in an example: All the mole ratios of Monomer II are 1:1.

[0038]

[Table 2]

表 2

	性 状				
	固 形 分 (%)	p H	粘 度 (c p s)	重量平均分子量	1 %濃度
実施例 1	15.7	3.0	3400	$320 \times 10^4$	透明
実施例 2	15.5	3.1	5800	$380 \times 10^4$	透明
実施例 3	15.6	3.0	5200	$350 \times 10^4$	透明
実施例 4	15.5	3.0	3700	$330 \times 10^4$	透明
比較例 1	15.4	3.0	4800	$300 \times 10^4$	透明
比較例 2	15.8	3.2	7000	$380 \times 10^4$	透明
比較例 3	15.5	3.0	6100	$340 \times 10^4$	透明
比較例 4	15.6	3.1	6500	$350 \times 10^4$	透明



[0039]

[Table 3]

表 3

	性 状			表2の粘度 に対する粘 度比
	p H	粘 度 (c p s)	1 %濃度	
実施例 1	4. 9	1 3 2 0 0	白濁	3. 9
実施例 2	4. 8	1 4 8 0 0	強白濁	2. 6
実施例 3	4. 9	1 4 2 0 0	白濁	2. 7
実施例 4	4. 8	1 1 2 0 0	強白濁	3. 0
比較例 1	4. 9	5 0 0 0	透明	1. 0
比較例 2	4. 9	7 5 0 0	透明	1. 1
比較例 3	5. 0	6 1 0 0	透明	1. 0
比較例 4	4. 8	6 6 0 0	透明	1. 0

[0040] Add and it is referred to as pH5.5. performance-evaluation approach 1 corrugated-paper used paper -- a Niagara style -- the pulp which carried out beating with the beater and which was adjusted to Canadian standard freeness (C. S.F) 420ml -- a sulfuric-acid band -- 1.6% for pulp -- It adds. subsequently, each copolymer water solution (pH3.0) obtained in each above-mentioned examples 1 and 2 and the examples 1 and 2 of a comparison -- a paper reinforcing agent -- carrying out -- 0.6% for pulp -- After agitating, pulp slurry concentration is diluted so that it may become 0.1%, and it is basis-weight 150 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 2 5kg/cm. Press dehydration was carried out for 2 minutes. after [ subsequently, / JIS ] drying for 3 minutes in 105 degrees C with a rotation mold dryer and carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0041] performance-evaluation approach 2 bleaching kraft pulp (BKP) -- a Niagara style -- each copolymer water solution obtained by the pulp (pH7.2) which carried out beating with the beater, and which was adjusted to C.S.F550ml in each above-mentioned examples 3 and 4 and the examples 3 and 4 of a comparison -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0042] performance-evaluation approach 3BKP -- a Niagara style -- the pulp which carried out beating with the beater and which was adjusted to C.S.F550ml -- a sulfuric-acid band -- 1.6% for pulp -- each copolymer water solution which added, set to pH5.5 and was subsequently obtained in each above-mentioned examples 1 and 2 and the examples 1 and 2 of a comparison -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0043] performance-evaluation approach 4BKP -- a Niagara style -- the pulp which carried out beating with the beater and which was adjusted to C.S.F550ml -- a sulfuric-acid band -- 1.6% for pulp, and a calcium carbonate -- 10% for pulp -- each copolymer water solution which added, set to pH7.5 and was subsequently obtained in each above-mentioned examples 3 and 4 and the examples 3 and 4 of a comparison -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0044]

[Table 4]

表 4

	評価方法 1	評価方法 2	評価方法 3	評価方法 4
実施例 1	2. 6 6	—	2. 8 8	—
実施例 2	2. 6 4	—	2. 9 0	—
実施例 3	—	2. 8 7	—	2. 5 6
実施例 4	—	2. 9 2	—	2. 4 5
比較例 1	2. 3 4	—	2. 2 9	—
比較例 2	2. 2 2	—	2. 3 6	—
比較例 3	—	2. 3 5	—	2. 1 8
比較例 4	—	2. 4 2	—	2. 0 5

[0045] From the result of Table 2 - 4, according to the acrylamide system copolymer which is used by this invention and which is a specific graft polymer (meta), though it is a high molecular weight object compared with elegance conventionally, having discovered the paper durability enhancing effect which is the almost same viscosity by about three pH, and was excellent when viscosity rose by about five pH is admitted. Moreover, forming the poly ion complex by pH 4-9 is admitted.

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TECHNICAL FIELD

[Industrial Application] This invention relates to the additive for paper manufacture. In detail, it is related with the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of graft structure.

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PRIOR ART

[Description of the Prior Art] In recent years, on the occasion of manufacture of paper and the paper board, importance has been attached to the additive for paper manufacture, especially the paper reinforcing agent. It is further raised with the purpose of energy saving or a deployment of a resource that use of good-quality pulp was restricted with aggravation of a bolt supply situation as this background and that the need for reuse of used paper became strong much more, and the additive for paper manufacture as a modifier of paper and the paper board is much more indispensable as that result.

[0003] On the other hand, the dependence and its use range of a filtration improvement agent and a paper reinforcing agent have spread further for the purpose of upgrading according to the improvement in the productivity accompanying improvement in the speed of a paper machine, or diversification of paper. As an additive for paper manufacture, a polyacrylamide system is in use under this situation.

[0004] The additive for polyacrylamide system paper manufacture can be classified into an anion type, a cation type, and a both-sexes type according to ionicity. For example, as this anion type, the partial hydrolysate of a copolymer with alpha [ which is acrylamide and an anionic vinyl monomer ], beta-partial saturation monocarboxylic acid or alpha, and beta-partial saturation dicarboxylic acid, or an acrylamide system copolymer etc. is known. On the other hand, as a cation type and a both-sexes type, there is a denaturation type and copolymerization type thing based on a difference of the introductory approach of an ionicity functional group. For example, as a denaturation type, there are a Hofmann rearrangement object of an acrylamide system copolymer, a MANNIHHI denaturation object, etc., and, on the other hand, the various copolymers which come to copolymerize a cationic vinyl monomer and the Nonion nature vinyl monomer which an anionic vinyl monomer or others may copolymerize acrylamide (meta) and if needed as a copolymerization type are known (JP,60-94697,A).

[0005] however, conventionally well-known in recent years, since the service condition of the additive for paper manufacture is becoming still severer -- it is coming to the limitation by the additive for polyacrylamide system paper manufacture of low molecular weight in respect of the effectiveness as an additive comparatively. Therefore, the means of macromolecule quantification is taken in order to aim at improvement in the engine performance, but since the viscosity of the copolymer obtained rises too much when macromolecule quantification is only carried out, the dispersibility at the time of paper making serves as a defect. Consequently, when this copolymer is used as an additive for paper manufacture, too much condensation arises, and it is easy to cause the conditions turbulence of perfect paper.

[0006] Although the attempt to which you are going to make it increase that molecular weight was made suppressing a viscosity rise of the copolymer obtained, the effectiveness as an additive for paper manufacture was not [ that this trouble should be canceled / that it is hard to introduce branching structure uniform in the reactivity of a cross linking agent being inadequate ] yet enough [ branching structure was given by using a cross linking agent, and ]. Moreover, although the approach of using the water solution which comes to mix the anionic Pori (meta) acrylamide and cationic Pori (meta) acrylamide of low molecular weight beforehand comparatively was also proposed, the effectiveness as an additive for paper manufacture was not yet enough.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The additive for paper manufacture which comes to contain the acrylamide system copolymer which has the graft structure of this invention (meta) is the copolymer of the amount of macromolecules in hypoviscosity, and shows the outstanding workability in paper making. moreover, in 4-9 which are paper making pH, that viscosity increases and since the firm poly ion complex is further formed in pH 4-9, the graft copolymer of this invention can raise [ high fixing of a between / pulp fiber /, high paper durability reinforcement, and ] filterability, without disturbing conditions further -- etc. -- the various characteristic engine performance as an additive for paper manufacture is shown.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention comes to contain the acrylamide (meta) system copolymer of the amount of macromolecules, and aims at offering the additive for paper manufacture whose engine performance is hypoviscosity comparatively and moreover improved by excelling in fixable [ to pulp ].

[0008]

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MEANS

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[Means for Solving the Problem] The result of having repeated research wholeheartedly this invention persons solving the technical problem of said conventional technique, According to the acrylamide (meta) system copolymer of the graft structure of the both-sexes type which gave the bias to the ion component which consists of an anionic polymer part and a cationic polymer part According to the copolymer of this graft structure, further it not only can obtain, without making the acrylamide (meta) system copolymer of the amount of macromolecules hyperviscosity-ize, but Viscosity changes depending on pH and from viscosity rising by 4-9 which are paper making pH when it is hypoviscosity by pH 2-3.5 notably This copolymer came to complete a header and this invention for excelling in fixable [ to pulp ] and excelling in many effectiveness, such as paper durability enhancement as an additive for paper manufacture, and filtration improvement.

[0009] Namely, the copolymer with which this invention comes to copolymerize (d) cross-linking vinyl monomer in (a) acrylamide and/or methacrylamide, (b) anionic vinyl monomer, and a list as a principal component (I), (a) Acrylamide and/or methacrylamide, (c) cationic vinyl monomer, It is the graft copolymer which comes to carry out the graft of the copolymer (II) which comes to copolymerize (d) cross-linking vinyl monomer as a principal component to a list. The weight average molecular weight of this graft copolymer is 1 million-5 million. And the ratio of the viscosity in pH 4-9 in this concentration starts the additive for paper manufacture which comes to contain the graft copolymer which are 1.5-6 to the viscosity in pH 2-3.5 in 15% concentration of this graft copolymer water solution.

[0010] In this invention, although it can be independent-used or the acrylamide or methacrylamide which is the (a) component can be used together, it is good to carry out independent use of the acrylamide from the field of economical efficiency.

[0011] As an anionic vinyl monomer which is the aforementioned (b) component, the sodium salt of organic sulfonic-acids [, such as dicarboxylic acid; vinyl sulfonic acids, such as monocarboxylic acid; maleic acids, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a fumaric acid, an itaconic acid, muconic acid and a citraconic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, ]; or these various organic acids, potassium salt, etc. are raised, for example, moreover, as a cationic vinyl monomer (c) For example, dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, Dimethylaminopropyl (meta) acrylamide, diethylamino propyl (meta) acrylamide, The vinyl monomers which have the third class amino groups, such as allylamine, a diaryl amine, or a triaryl amine, or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content vinyl monomer and methyl chloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the fourth class-ized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised. These ionicity vinyl monomer is independent in a kind, or can use two or more sorts together.

[0012] (d) As a cross-linking vinyl monomer which is a component For example, ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene screw

(meta) acrylamide, Screw (meta) acrylamides, such as hexa methylenebis (meta) acrylamide Divinyl ester, such as an adipic-acid divinyl and a sebacic-acid divinyl Allyl compound methacrylate, epoxy acrylate, and urethane acrylate N-methylol acrylamide, a diaryl amine, diaryl dimethylammonium, 2 functionality vinyl monomers, such as diallyl phthalate, diallyl chlorendate, and a divinylbenzene, 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, 3 functionality monomers, such as triaryl amine, triallyl trimellitate, N, and N-diaryl acrylamide, 4 functionality vinyl monomers, such as tetramethylolmethane tetraacrylate, tetra-allyl compound pyromellitate, N and N, N', and N'-tetra-allyl compound-1,4-diaminobutane, a tetra-allylamine salt, and tetra-allyloxy ethane, etc. are raised.

[0013] Moreover, as a cross-linking vinyl monomer of this invention, the vinyl monomer which has a chain transfer nature substituent can be used. As a vinyl monomer which has a chain transfer nature substituent, if it has a chain transfer nature functional group, a vinyl monomer, itaconic-acid diester, etc. which can use it without a limit, for example, have an allyl group, a polyalkylene glycol radical, N-permutation amide group, etc. will be raised especially. As a vinyl monomer which has an allyl group, allyl compound (meta) acrylate, N-allyl compound (meta) acrylamide, N, and N-diaryl (meta) acrylamide etc. is mentioned. Moreover, the thing to about ten repeat units can usually be used that what is necessary is just what has the repeat unit of at least two oxy-alkylene groups as a polyalkylene glycol radical. As an example, diethylene-glycol monochrome (meta) acrylate,



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## EXAMPLE

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. In addition, each of sections and %s is based on weight criteria.

[0029] The ion-exchange-water 509 section was taught to the 6 opening flask equipped with example 1 agitator, a thermometer, a reflux cooling pipe, two dropping funnels, and nitrogen gas installation tubing, the oxygen in the system of reaction was removed in it through nitrogen gas, and the temperature up was carried out to it to 100 degrees C.

[0030] Subsequently, as a monomer I, the acrylamide 95.5 section, the ion-exchange-water 304 section, the 50% sulfuric-acid 11.7 section, the dimethylaminoethyl methacrylate 23.4 section, and the dimethyl acrylamide 0.2 section were taught to the dropping funnel, and the oxygen in the system of reaction was removed through nitrogen gas.

[0031] Moreover, to another dropping funnel, as a monomer II, the acrylamide 95.5 section, the ion-exchange-water 304 section, the 80% acrylic-acid water-solution 13.4 section, and the dimethyl acrylamide 0.2 section were taught, and the oxygen in the system of reaction was removed through nitrogen gas.

[0032] Moreover, the ammonium persulfate 0.5 section and the ion-exchange-water 90 section were taught to another dropping funnel as a polymerization initiator.

[0033] While keeping the inside of a system at 95-100 degrees C and dropping the polymerization initiator at the bottom of churning of 300rpm, after dropping and carrying out copolymerization of the above-mentioned monomer I, the above-mentioned monomer II was dropped and the polymerization was performed for 2 hours. It cooled after 1-hour incubation. The description at the time of Table 2 and about five pH is shown for the description at the time of about three pH of the obtained copolymer water solution in Table 3.

[0034] In two to example 4 example 1, among the class of (a) component - (e) component, or its amount used, in any, at least one sort was changed, as shown in Table 1, and also the same actuation as an example 1 was performed, and the graft copolymer water solution was obtained. The description according to pH of each obtained copolymer water solution is shown in Table 2 and 3. In addition, a visual judgment of the condition at the time of diluting the obtained copolymer water solution to concentration 1% was made with "1% concentration" of Table 2 and 3.

[0035] In one to example of comparison 4 examples 1-4, the polymerization of the monomer of Monomer I and Monomer II was carried out to coincidence, and also the same actuation as an example 1 was performed. The description according to pH of the obtained copolymer water solution is shown in Table 2 and 3.

[0036]

[Table 1]

表 1

		組 成 (モル%)				
		(a)	(b)	(c)	(d)	(e)
実施例 1	モノマー I	AM 88.8	—	DM 10.1	DMAA 0.1	—
	モノマー II	AM 89.9	AA 10.0	—	DMAA 0.1	—
実施例 2	モノマー I	AM 84.9	—	DM 10.0	DMAA 0.1	AN 5.0
	モノマー II	AM 84.9	AA 10.0	—	DMAA 0.1	AN 5.0
実施例 3	モノマー I	AM 85.0	—	DMAPAA 9.9	DMAA 0.1	—
	モノマー II	AM 84.9	AA 10.0	—	DMAA 0.1	—
実施例 4	モノマー I	AM 85.0	—	DMAPAA 9.9	DMAA 0.1	AN 5.0
	モノマー II	AM 84.9	AA 10.0	—	DMAA 0.1	AN 5.0
比較例 1	—	AM 89.9	AA 5	DM 5	DMAA 0.1	—
比較例 2	—	AM 84.9	AA 5	DM 5	DMAA 0.1	AN 5
比較例 3	—	AM 89.9	AA 5	DMAPAA 5	DMAA 0.1	—
比較例 4	—	AM 84.9	AA 5	DMAPAA 5	DMAA 0.1	AN 5

[0037] the inside of Table 1, and AM -- acrylamide -- DM -- dimethylaminoethyl methacrylate -- DMAPAA -- dimethylaminopropyl acrylamide -- in AA, DMAA shows dimethyl acrylamide and AN shows acrylonitrile for an acrylic acid, respectively. Moreover, each monomer I in an example: All the mole ratios of Monomer II are 1:1.

[0038]

[Table 2]

表 2

	性 状				
	固 形 分 (%)	p H	粘 度 (c p s)	重量平均分子量	1%濃度
実施例 1	15.7	3.0	3400	$320 \times 10^4$	透明
実施例 2	15.5	3.1	5800	$380 \times 10^4$	透明
実施例 3	15.6	3.0	5200	$350 \times 10^4$	透明
実施例 4	15.5	3.0	3700	$330 \times 10^4$	透明
比較例 1	15.4	3.0	4800	$300 \times 10^4$	透明
比較例 2	15.8	3.2	7000	$380 \times 10^4$	透明
比較例 3	15.5	3.0	6100	$340 \times 10^4$	透明
比較例 4	15.6	3.1	6500	$350 \times 10^4$	透明

[0039]

[Table 3]

表 3

	性 状			表2の粘度 に対する粘 度比
	p H	粘 度 ( c p s )	1 %濃度	
実施例 1	4. 9	1 3 2 0 0	白濁	3. 9
実施例 2	4. 8	1 4 8 0 0	強白濁	2. 6
実施例 3	4. 9	1 4 2 0 0	白濁	2. 7
実施例 4	4. 8	1 1 2 0 0	強白濁	3. 0
比較例 1	4. 9	5 0 0 0	透明	1. 0
比較例 2	4. 9	7 5 0 0	透明	1. 1
比較例 3	5. 0	6 1 0 0	透明	1. 0
比較例 4	4. 8	6 6 0 0	透明	1. 0

[0040] Add and it is referred to as pH5.5. performance-evaluation approach 1 corrugated-paper used paper -- a Niagara style -- the pulp which carried out beating with the beater and which was adjusted to Canadian standard freeness (C. S.F) 420ml -- a sulfuric-acid band -- 1.6% for pulp -- It adds. subsequently, each copolymer water solution (pH3.0) obtained in each above-mentioned examples 1 and 2 and the examples 1 and 2 of a comparison -- a paper reinforcing agent -- carrying out -- 0.6% for pulp -- After agitating, pulp slurry concentration is diluted so that it may become 0.1%, and it is basis-weight 150 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 2 5kg/cm. Press dehydration was carried out for 2 minutes. after [ subsequently, / JIS ] drying for 3 minutes in 105 degrees C with a rotation mold dryer and carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0041] performance-evaluation approach 2 bleaching kraft pulp (BKP) -- a Niagara style -- each copolymer water solution obtained by the pulp (pH7.2) which carried out beating with the beater, and which was adjusted to C.S.F550ml in each above-mentioned examples 3 and 4 and the examples 3 and 4 of a comparison -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0042] performance-evaluation approach 3BKP -- a Niagara style -- the pulp which carried out beating with the beater and which was adjusted to C.S.F550ml -- a sulfuric-acid band -- 1.6% for pulp -- each copolymer water solution which added, set to pH5.5 and was subsequently obtained in each above-mentioned examples 1 and 2 and the examples 1 and 2 of a comparison -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0043] performance-evaluation approach 4BKP -- a Niagara style -- the pulp which carried out beating with the beater and which was adjusted to C.S.F550ml -- a sulfuric-acid band -- 1.6% for pulp, and a calcium carbonate -- 10% for pulp -- each copolymer water solution which added, set to pH7.5 and was subsequently obtained in each above-mentioned examples 3 and 4 and the examples 3 and 4 of a comparison -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 4.

[0044]

[Table 4]

表 4

	評価方法 1	評価方法 2	評価方法 3	評価方法 4
実施例 1	2. 6 6	—	2. 8 8	—
実施例 2	2. 6 4	—	2. 9 0	—
実施例 3	—	2. 8 7	—	2. 5 6
実施例 4	—	2. 9 2	—	2. 4 5
比較例 1	2. 3 4	—	2. 2 9	—
比較例 2	2. 2 2	—	2. 3 6	—
比較例 3	—	2. 3 5	—	2. 1 8
比較例 4	—	2. 4 2	—	2. 0 5

[0045] From the result of Table 2 - 4, according to the acrylamide system copolymer which is used by this invention and which is a specific graft polymer (meta), though it is a high molecular weight object compared with elegance conventionally, having discovered the paper durability enhancing effect which is the almost same viscosity by about three pH, and was excellent when viscosity rose by about five pH is admitted. Moreover, forming the poly ion complex by pH 4-9 is admitted.

[Translation done.]